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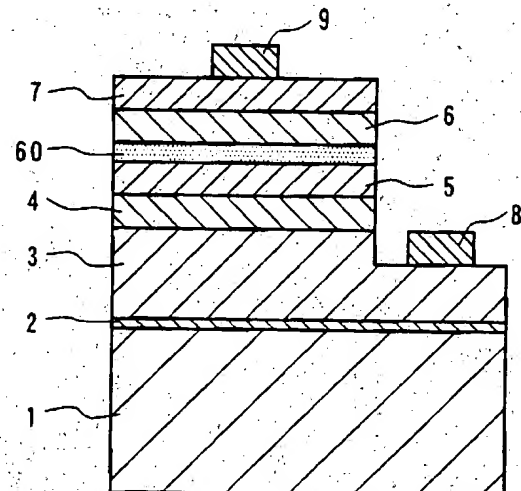
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(54) 【発明の名称】 窒化物半導体発光素子

(57) 【要約】

【目的】 静電耐圧が大きい窒化物半導体発光素子を実現して、窒化物半導体発光素子の信頼性を向上させる。  
 【構成】 単一量子井戸もしくは多重量子井戸構造を有する活性層と、n型クラッド層との間に、インジウムを含むn型の窒化物半導体よりなる第二のn型クラッド層を有し、さらに前記活性層と、p型クラッド層との間に、少なくともインジウムを含むp型の窒化物半導体、またはp型のGa Nよりなる第二のp型クラッド層が形成されている。



## 【特許請求の範囲】

【請求項1】 単一量子井戸もしくは多重量子井戸構造を有する活性層と、n型クラッド層との間に、インジウムを含むn型の窒化物半導体よりなる第二のn型クラッド層を有し、さらに前記活性層と、p型クラッド層との間に、少なくともインジウムを含むp型の窒化物半導体、またはp型のGa<sub>1-x</sub>Nよりなる第二のp型クラッド層が形成されていることを特徴とする窒化物半導体発光素子。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】 本発明は発光ダイオード(LED)、レーザダイオード(LD)等に使用される窒化物半導体(In<sub>a</sub>Al<sub>b</sub>Ga<sub>1-a-b</sub>N、0≤a、0≤b、a+b≤1)よりなる発光素子に係り、特にダブルヘテロ構造を有する窒化物半導体発光素子に関する。

## 【0002】

【従来の技術】 紫外～赤色に発光するLED、LD等の発光素子の材料として窒化物半導体(In<sub>a</sub>Al<sub>b</sub>Ga<sub>1-a-b</sub>N、0≤a、0≤b、a+b≤1)が知られている。我々はこの半導体材料を用いて、1993年11月に光度1cdの青色LEDを発表し、1994年4月に光度2cdの青緑色LEDを発表し、1994年10月には光度2cdの青色LEDを発表した。これらのLEDは全て製品化されて、現在ディスプレイ、信号等の実用に供されている。

【0003】 図2に窒化物半導体よりなる従来の青色、青緑色LEDの発光チップの構造を示す。基本的には、基板21の上に、Ga<sub>1-x</sub>Nよりなるバッファ層22、n型Ga<sub>1-x</sub>Nよりなるn型コンタクト層23と、n型AlGa<sub>1-x</sub>Nよりなるn型クラッド層24と、n型InGa<sub>1-x</sub>Nよりなる活性層25と、p型AlGa<sub>1-x</sub>Nよりなるp型クラッド層26と、p型Ga<sub>1-x</sub>Nよりなるp型コンタクト層27とが順に積層された構造を有している。活性層25のn型InGa<sub>1-x</sub>NにはSi、Ge等のドナー不純物および/またはZn、Mg等のアクセプター不純物がドーパされており、LED素子の発光波長は、その活性層のInGa<sub>1-x</sub>NのIn組成比を変更するか、若しくは活性層にドーパする不純物の種類を変更することで、紫外～赤色まで変化させることが可能となっている。今のところ、活性層にドナー不純物とアクセプター不純物とが同時にドーパされた発光波長510nm以下のLEDが実用化されている。

## 【0004】

【発明が解決しようとする課題】 従来のLEDは順方向電流20mAで発光出力は3mW近くあり、SiCよりなるLEDと比較して20倍以上の出力を有している。しかしながらこのLEDは静電耐圧が低く、例えば逆方向でバイアスして測定するとおよそ50～100Vしかないという欠点があった。静電耐圧が低いと乾燥した雰

囲気中でLEDを取り扱ったとき、容易に静電気により素子が破壊されるので、信頼性に乏しい。

【0005】 従って、本発明はこのような事情を鑑みて成されたものであって、その目的とするところは静電耐圧が大きい窒化物半導体発光素子及び高出力な発光素子を実現して、窒化物半導体発光素子の信頼性を向上させることにある。

## 【0006】

【課題を解決するための手段】 我々は従来のダブルヘテロ構造の窒化物半導体発光素子について、種々の実験を重ねた結果、活性層の次に成長させるp型クラッド層に、その原因の多くがあることを突き止め、本発明を成すに至った。即ち、本発明の窒化物半導体発光素子は、単一量子井戸もしくは多重量子井戸構造を有する活性層と、n型クラッド層との間に、インジウムを含むn型の窒化物半導体よりなる第二のn型クラッド層を有し、さらに前記活性層と、p型クラッド層との間に、少なくともインジウムを含むp型の窒化物半導体、またはp型のGa<sub>1-x</sub>Nよりなる第二のp型クラッド層が形成されていることを特徴とする。

【0007】 図1は本発明の一実施例に係る発光素子の構造を示す模式断面図である。この発光素子は基板1の上にバッファ層2、n型コンタクト層3、n型クラッド層4、活性層5、第二のp型クラッド層6、第一のp型クラッド層7、p型コンタクト層8を順に積層した構造を示している。

【0008】 基板1にはサファイア(A面、C面、R面を含む)の他、SiC(6H、4Hを含む)、ZnO、Si、GaAsのような窒化物半導体と格子不整合の基板、またNGO(ネオジムガレート)のような酸化物単結晶よりなる窒化物半導体と格子定数の近い基板等を使用することができる。

【0009】 バッファ層2はGa<sub>1-x</sub>N、AlN、GaAlN等を例えば500Å～0.1μmの膜厚で成長させることが好ましく、例えばMOVPE法によると400℃～600℃の低温で成長させることにより形成できる。

【0010】 n型コンタクト層3は負電極8を形成する層であり、Ga<sub>1-x</sub>N、AlGa<sub>1-x</sub>N、InAlGa<sub>1-x</sub>N等を例えば1μm～10μmの膜厚で成長させることが好ましく、その中でもGa<sub>1-x</sub>Nを選択することにより負電極の材料と好ましいオーミック接触を得ることができる。負電極8の材料としては例えばAl、Au、Ti等を好ましく用いることができる。

【0011】 n型クラッド層4はGa<sub>1-x</sub>N、AlGa<sub>1-x</sub>N、InAlGa<sub>1-x</sub>N等を例えば500Å～0.5μmの膜厚で成長させることが好ましく、その中でもGa<sub>1-x</sub>N、AlGa<sub>1-x</sub>Nを選択することにより結晶性の良い層が得られる。また、n型クラッド層4、n型コンタクト層3のいずれかを省略することも可能である。ど

ちらかを省略すると、残った層がn型クラッド層およびn型コンタクト層として作用する。

【0012】活性層5はクラッド層よりもバンドギャップエネルギーが小さいInGa<sub>N</sub>、InAlGa<sub>N</sub>、AlGa<sub>N</sub>等の窒化物半導体であれば良く、特に所望のバンドギャップによってインジウムの組成比を適宜変更したInGa<sub>N</sub>にすることが好ましい。また活性層5を例えばInGa<sub>N</sub>/Ga<sub>N</sub>、InGa<sub>N</sub>/InGa<sub>N</sub>（組成が異なる）等の組み合わせで、それぞれの薄膜を積層した多重量子井戸構造としてもよい。単一量子井戸構造、多重量子井戸構造いずれの活性層においても、活性層はn型、p型いずれでもよいが、特にノンドープ（無添加）とすることにより半値幅の狭いバンド間発光、励起子発光、あるいは量子井戸準位発光が得られ、LED素子、LD素子を実現する上で特に好ましい。活性層を単一量子井戸（SQW: single quantum well）構造若しくは多重量子井戸（MQW: multi quantum well）構造とすると非常に出力の高い発光素子が得られる。SQW、MQWとはノンドープのInGa<sub>N</sub>による量子準位間の発光が得られる活性層の構造を指し、例えばSQWでは活性層を単一組成のIn<sub>x</sub>Ga<sub>1-x</sub>N（0 ≤ x < 1）で構成した層であり、In<sub>x</sub>Ga<sub>1-x</sub>Nの膜厚を100オングストローム以下、さらに好ましくは70オングストローム以下とすることにより量子準位間の強い発光が得られる。またMQWは組成比の異なるIn<sub>x</sub>Ga<sub>1-x</sub>N（この場合x=0、x=1を含む）の薄膜を複数積層した多層膜とする。このように活性層をSQW、MQWとすることにより量子準位間発光で、約365nm～660nmまでの発光が得られる。量子構造の井戸層の厚さとしては、前記のように70オングストローム以下が好ましい。多重量子井戸構造では井戸層はIn<sub>x</sub>Ga<sub>1-x</sub>Nで構成し、障壁層は同じくIn<sub>y</sub>Ga<sub>1-y</sub>N（y < x、この場合y=0を含む）で構成することが望ましい。特に好ましくは井戸層と障壁層をInGa<sub>N</sub>で形成すると同一温度で成長できるので結晶性のよい活性層が得られる。障壁層の膜厚は150オングストローム以下、さらに好ましくは120オングストローム以下にすると高出力の発光素子が得られる。また、活性層5にドナー不純物および/またはアクセプター不純物をドーピングしてもよい。不純物をドーピングした活性層の結晶性がノンドープと同じであれば、ドナー不純物をドーピングするとノンドープのものに比べてバンド間発光強度をさらに強くすることができる。アクセプター不純物をドーピングするとバンド間発光のピーク波長よりも約0.5eV低エネルギー側にピーク波長を持っていくことができるが、半値幅は広がる。アクセプター不純物とドナー不純物を同時にドーピングすると、アクセプター不純物のみドーピングした活性層の発光強度をさらに大きくすることができる。特にアクセプター不純物をドーピングした活性層を実現する場合、活性層の導電型はSi等のドナー不純物を同時にドーピングしてn型と

することが好ましい。活性層5は例えば数オングストローム～0.5μmの膜厚で成長させることができる。但し、活性層をSQW、若しくはMQWとするときは、n型クラッド層4と活性層5との間にInを含むn型の窒化物半導体、またはn型Ga<sub>N</sub>よりなる第二のn型クラッド層を形成することが望ましい。

【0013】次に本発明の最も特徴である第二のp型クラッド層60は少なくともインジウムを含むp型の窒化物半導体（In<sub>x</sub>Al<sub>y</sub>Ga<sub>1-x-y</sub>N、0 < x, y ≤ 0, x+y < 1）またはp型のGa<sub>N</sub>で形成する必要がある。その中でもInGa<sub>N</sub>、またはGa<sub>N</sub>等のAlを含まない窒化物半導体で形成することが特に好ましい。さらに第二のp型クラッド層60の膜厚は200オングストローム以下、さらに好ましくは100オングストローム以下の膜厚で形成することが好ましい。なぜなら、200オングストローム以下の膜厚に調整することにより、発光素子の発光出力をほとんど維持したまま、発光素子の静電耐圧を上げることが可能となるからである。逆にその膜厚が200オングストロームよりも厚いと、発光素子の出力が低下する傾向にある。

【0014】第一のp型クラッド層6はGa<sub>N</sub>、AlGa<sub>N</sub>、InAlGa<sub>N</sub>等を例えば500オングストローム～0.5μmの膜厚で成長させることが好ましく、その中でもGa<sub>N</sub>、AlGa<sub>N</sub>を選択することにより結晶性の良い層が得られる。また、第二のp型クラッド層60の組成と第一のp型クラッド層6の組成が同じである場合、第一のp型クラッド層6の組成比を変化させて、バンドギャップエネルギーを第二のp型クラッド層60と同じとするか、または大きくする。

【0015】p型コンタクト層7は正電極9を形成する層であり、例えばGa<sub>N</sub>、AlGa<sub>N</sub>、InAlGa<sub>N</sub>等を成長させることが好ましく、その中でもGa<sub>N</sub>を選択することにより正電極の材料と好ましいオーミック接触を得ることができる。正電極材料としてはNi、Au等を好ましく用いることができる。また、p型コンタクト層7、第一のp型クラッド層6のいずれかを省略することも可能である。どちらかを省略すると、残った層が第一のp型クラッド層およびp型コンタクト層として作用する。

【0016】本発明の発光素子は例えばMOVPE（有機金属気相成長法）、MBE（分子線気相成長法）、HDVPE（ハイドライド気相成長法）等の気相成長法を用いて、基板上にIn<sub>a</sub>Al<sub>b</sub>Ga<sub>1-a-b</sub>N（0 ≤ a, 0 ≤ b, a+b ≤ 1）をn型、p型等の導電型で積層することによって得られる。n型の窒化物半導体はノンドープの状態でも得られるが、Si、Ge、S等のドナー不純物を結晶成長中に半導体層中に導入することによって得られる。これらのドナー不純物濃度を調整することにより、n型層のキャリア濃度を調整できる。一方、p型の窒化物半導体層はMg、Zn、Cd、Ca、Be、C等

のアクセプター不純物を同じく結晶成長中に半導体層中に導入するか、または導入後400℃以上でアニーリングを行うことにより得られる。同様にこれらアクセプター不純物濃度を調整することにより、p型層のキャリア濃度を調整することができる。バッファ層2は基板1と窒化物半導体との格子不整合を緩和するために設けられるが、SiC、ZnOのような窒化物半導体と格子定数が近い基板、窒化物半導体と格子整合した基板を使用する際にはバッファ層が形成されないこともある。

【0017】

【作用】従来のLEDでは例えばInを含む活性層の上にAlを含む第一のp型クラッド層を成長させていた。一方、本発明では新たに活性層と第一のp型クラッド層との間にGaNまたはInを含む窒化物半導体よりなる第二のp型クラッド層を成長させている。この構成により発光素子の静電耐圧を向上させることができる。これは活性層の上の第二のp型クラッド層がバッファ層の作用をして、第一のp型クラッド層の結晶性を良くして素子の静電耐圧を向上させている。窒化物半導体はバンドギャップエネルギーの大きい順、 $AlN > GaN > InN$ の順に結晶自体が柔らかい性質を持っている。つまり、Inを含む窒化物半導体、またはGaNよりなる第二のp型クラッド層は、第二のp型クラッド層よりもバンドギャップエネルギーが大きい第一のp型クラッド層に比べて結晶自体が柔らかい。この柔らかい結晶である第二のp型クラッド層がバッファ層の作用をすることにより、その第二のp型クラッド層の上に成長させる第一のp型クラッド層の結晶性が良くなり、格子欠陥が少なくなるので、素子全体の静電耐圧が向上するのである。

【0018】バッファ層として好適に作用する第二のp型クラッド層の膜厚は200オングストローム以下が好ましい。第二のp型クラッド層を厚く積むほど静電耐圧は向上する傾向にあるが、膜厚が厚すぎると、その第二のp型クラッド層自体に結晶欠陥が多く発生してしまいバッファ層として作用しにくくなる傾向にある。結晶欠陥の多い第二のp型クラッド層の上に第一のp型クラッド層を成長させると、結晶欠陥が第一のp型クラッド層にまで伝わってしまうので、結晶性の良い第一のp型クラッド層が成長しにくくなる。このため第二のp型クラッド層の膜厚が厚すぎると、発光素子の出力が低下する傾向にある。第二のp型クラッド層の膜厚の下限は特に限定するものではなく、例えば1原子層、2原子層にあたるような数オングストロームの膜厚で形成してもよい。

【0019】

【実施例】以下本発明を具体的な実施例に基づいて説明する。以下の実施例はMOVPE法による成長方法を示している。

【0020】【実施例1】図1を元に実施例1について説明する。まず、TMG（トリメチルガリウム）とNH

3とを用い、反応容器にセットしたサファイア基板1のC面に500℃でGaNよりなるバッファ層2を500オングストロームの膜厚で成長させる。

【0021】次に温度を1050℃まで上げ、TMG、NH<sub>3</sub>に加えシランガスを用い、Siドープn型GaNよりなるn型コンタクト層23を4μmの膜厚で成長させる。

【0022】続いて原料ガスにTMA（トリメチルアルミニウム）を加え、同じく1050℃でSiドープn型Al<sub>0.3</sub>Ga<sub>0.7</sub>N層よりなるn型クラッド層4を0.1μmの膜厚で成長させる。

【0023】次に温度を800℃に下げ、TMG、TMI（トリメチルインジウム）、NH<sub>3</sub>、シランガス、DEZ（ジエチルジシラン）を用い、Si+Znドープn型In<sub>0.05</sub>Ga<sub>0.95</sub>Nよりなる活性層5を0.1μmの膜厚で成長させる。

【0024】続いて800℃にて、TMG、TMI（トリメチルインジウム）、NH<sub>3</sub>、Cp2Mg（シクロペンタジエニルマグネシウム）ガスを用い、Mgドープp型In<sub>0.01</sub>Ga<sub>0.99</sub>Nよりなる第二のp型クラッド層60を50オングストローム成長させる。

【0025】次に温度を1050℃に上げ、TMG、TMA、NH<sub>3</sub>、Cp2Mg（シクロペンタジエニルマグネシウム）を用い、Mgドープp型Al<sub>0.3</sub>Ga<sub>0.7</sub>Nよりなる第一のp型クラッド層6を0.1μmの膜厚で成長させる。

【0026】続いて1050℃でTMG、NH<sub>3</sub>、Cp2Mgを用い、Mgドープp型GaNよりなるp型コンタクト層7を0.5μmの膜厚で成長させる。

【0027】反応終了後、温度を室温まで下げてウェーハを反応容器から取り出し、700℃でウェーハのアニーリングを行い、p型層をさらに低抵抗化する。次に最上層のp型コンタクト層7の表面に所定の形状のマスクを形成し、n型コンタクト層3の表面が露出するまでエッチングする。エッチング後、n型コンタクト層3の表面にTiとAlよりなる負電極8、p型コンタクト層7の表面にNiとAuよりなる正電極9を形成する。電極形成後、ウェーハを350μm角のチップに分離した後、LED素子とした。このLED素子はIf 20mAでVf 3.6V、発光ピーク波長450nm、半値幅70nmの青色発光を示し、発光出力は3mWであった。さらに、このLEDの両電極に逆バイアスをかけて静電耐圧を測定したところ、400Vまで素子が破壊しなかった。

【0028】【実施例2】第二のp型クラッド層60の膜厚を100オングストロームとする他は実施例1と同様にLED素子を得たところ、発光出力は3mWと同一で、静電耐圧は450Vまで向上していた。

【0029】【実施例3】第二のp型クラッド層60の膜厚を200オングストロームとする他は実施例1と同

様にしてLED素子を得たところ、発光出力は2.5mW、静電耐圧は550Vまで向上していた。

【0030】[実施例4] 第二のp型クラッド層60の膜厚を300オングストロームとする他は実施例1と同様にしてLED素子を得たところ、静電耐圧は650Vまで向上したが、発光出力は1mWまで低下した。

【0031】[実施例5] 第二のp型クラッド層60にMgドープp型Ga<sub>0.99</sub>Nを10オングストロームの膜厚で形成する他は実施例1と同様にしてLED素子を得たところ、発光出力は実施例1と同じ3mW、静電耐圧は360Vであった。

【0032】[実施例6] 図3は実施例6に係る発光素子の構造を示す模式的な断面図である。この発光素子が図1の発光素子と異なるところは、n型クラッド層4と活性層5との間に新たなバッファ層としてInを含むn型の窒化物半導体、またはn型Ga<sub>0.99</sub>Nよりなる第二のn型クラッド層40を形成しているところである。この第二のクラッド層40は10オングストローム以上、0.1μm以下の膜厚で形成することが望ましく、さらに第二のn型クラッド層40と活性層5の膜厚を300オングストローム以上にすると、Inを含む第一のn型クラッド層40とInを含む活性層5とがバッファ層として作用し、n型クラッド層4、p型クラッド層6にクラックが入らず結晶性良く成長できる。さらに、この第二のn型クラッド層40を成長させることにより、不純物をドーピングしない活性層が実現でき、半値幅が狭く、出力の高い発光を得ることができる。

【0033】この第二のn型クラッド層40は、活性層5とAlとGaとを含むn型クラッド層4との間のバッファ層として作用する。つまりInとGaとを含む第二のn型クラッド層40が結晶の性質として柔らかい性質を有しているので、AlとGaとを含むn型クラッド層4と活性層5との格子定数不整と熱膨張係数差によって生じる歪を吸収する働きがある。従って活性層5を膜厚が薄い量子構造を有するSQW、MQWとしても、活性層5、n型クラッド層4にクラックが入らないので、活性層を量子構造にしても活性層が弾性的に変形し、活性層の結晶欠陥が少なくなる。つまり活性層の膜厚が薄い状態においても、活性層の結晶性が良くなるので発光出力が増大する。さらに、活性層は膜厚を薄くしたことにより量子効果および励起子効果により発光出力が増大する。言い換えると、従来の発光素子では単一の活性層の膜厚を例えば1000オングストローム以上と厚くすることにより、クラッド層、活性層にクラックが入るのを防止していた。しかしながら活性層には常に熱膨張係数差、格子不整による歪が係っており、従来の発光素子では活性層の厚さが弾性的に変形可能な臨界膜厚を超えているので、弾性的に変形することができず、活性層中に多数の結晶欠陥を生じ、バンド間発光ではあまり光らない。この第二のn型クラッド層40を形成することによ

り、量子構造の活性層において、発光素子の発光出力を飛躍的に向上させることが可能である。

【0034】具体的には、実施例1においてn型クラッド層4を成長させた後、温度を800℃に下げ、TMG、TMI（トリメチルインジウム）、NH<sub>3</sub>、シランガスを用い、Siドープn型In<sub>0.01</sub>Ga<sub>0.99</sub>Nよりなる第二のn型クラッド層40を500オングストロームの膜厚で成長させる。

【0035】続いてTMG、TMI、NH<sub>3</sub>を用い800℃でノンドープn型In<sub>0.05</sub>Ga<sub>0.95</sub>Nよりなる単一量子井戸構造の活性層5を80オングストロームの膜厚で成長させる。後は実施例1と同様にして、第二のp型クラッド層60と、第一のp型クラッド層6、p型コンタクト層7を成長させてLED素子としたところ、このLED素子は、If 20mAでVf 3.2V、発光ピーク波長400nmの青色発光を示し、発光出力は12mWであった。さらに、発光スペクトルの半値幅は20nmであり、非常に色純度の良い発光を示した。また静電耐圧も実施例1と同様に400Vであった。

【0036】[実施例7] 実施例6において、活性層5の組成をノンドープIn<sub>0.05</sub>Ga<sub>0.95</sub>Nよりなる井戸層を25オングストロームと、ノンドープIn<sub>0.01</sub>Ga<sub>0.99</sub>Nよりなる障壁層を50オングストロームの膜厚で成長させる。この操作を13回繰り返して、最後に井戸層を積層して総厚1000オングストロームの活性層6を成長させた。後は実施例1と同様にして、第二のp型クラッド層60と、第一のp型クラッド層6、p型コンタクト層7を成長させてLED素子としたところ、このLED素子は、If 20mAでVf 3.2V、発光ピーク波長400nmの青色発光を示し、発光出力は12mWであった。さらに、発光スペクトルの半値幅は20nmであり、非常に色純度の良い発光を示した。また静電耐圧は500Vであった。これは単一量子井戸構造の活性層よりも、多重量子井戸構造の活性層を有する素子の方が静電耐圧が高いことを示している。

【0037】[実施例8] 活性層5の膜厚を500オングストロームとする他は実施例6と同様にしてLED素子を得たところ、このLED素子は活性層の膜厚が厚くなったので、発光出力は3mWまで低下したが、発光ピーク波長390nmで、半値幅20nmの青色発光を示し、静電耐圧は400Vであった。

【0038】[実施例9] 第二のp型クラッド層60の膜厚を200オングストロームとする他は実施例6と同様にしてLED素子を得たところ、実施例6と同じく発光ピーク波長400nm、半値幅20nmの青色発光を示し、発光出力は10mW、静電耐圧は550Vまで向上していた。

【0039】

【発明の効果】従来の窒化物半導体発光素子では静電耐圧に弱く、特に乾燥した環境中では静電気により容易に

素子が破壊してしまい信頼性に乏しかった。しかし本発明により発光素子の静電耐圧が向上するので、素子が容易に破壊されにくくなり信頼性が極めて向上した。

【図面の簡単な説明】

【図1】 本発明の一実施例に係る発光素子の構造を示す模式断面図。

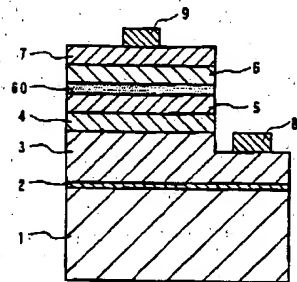
【図2】 従来の発光素子の構造を示す模式断面図。

【図3】 本発明の他の実施例に係る発光素子の構造を示す模式断面図。

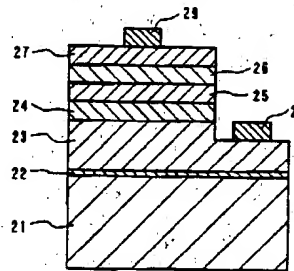
【符号の説明】

- 1 . . . . . 基板
- 2 . . . . . バッファ層
- 3 . . . . . n型コンタクト層
- 4 . . . . . n型クラッド層
- 5 . . . . . 活性層
- 6 . . . . . 第二のp型クラッド層
- 6 . . . . . 第一のp型クラッド層
- 7 . . . . . p型コンタクト層
- 8 . . . . . 負電極
- 9 . . . . . 正電極

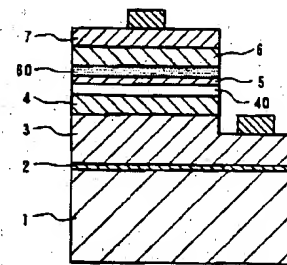
【図1】



【図2】



【図3】



(19)



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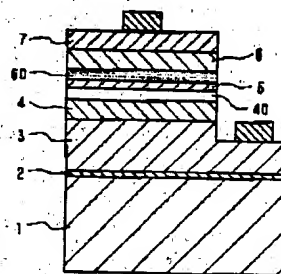
(72) Inventor:

**NAKAMURA SHUJI**(54) **NITRIDE SEMICONDUCTOR LIGHT-EMITTING ELEMENT**

(57) Abstract:

**PROBLEM TO BE SOLVED:** To improve the reliability of a nitride semiconductor light-emitting element by realizing the nitride semiconductor light-emitting element having a large electrostatic breakdown voltage.

**SOLUTION:** A second n-type clad layer 40 containing indium and consisting of an n-type nitride semiconductor is formed between an active layer 5 which has single quantum well or multiple quantum well structure and an n-type clad layer 4, and a second p-type clad layer 60 composed of a p-type nitride semiconductor containing at least indium or p-type GaN is formed between the active layer 5 and the p-type clad layer 6.



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 CLAIMS
 

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- [Claim(s)]

[Claim 1] The p type nitride semiconductor characterized by providing the following, or the nitride semiconductor light emitting device characterized by forming second p type clad layer which consists of p type GaN. The barrier layer which has a single quantum well or multiplex quantum well structure. It has second n type clad layer which consists of an n type nitride semiconductor which contains an indium between n type clad layers, and is the aforementioned barrier layer further. Between p type clad layers, it is an indium at least.

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 DETAILED DESCRIPTION
 

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[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the nitride semiconductor light emitting device which starts the light emitting device which consists of a nitride semiconductor ( $\text{In}_a\text{Al}_b\text{Ga}_{1-a-b}\text{N}$ ,  $0 \leq a$ ,  $0 \leq b$ ,  $a+b \leq 1$ ) used for light emitting diode (Light Emitting Diode), a laser diode (LD), etc., especially has terrorism structure to double.

[0002]

[Description of the Prior Art] The nitride semiconductor ( $\text{In}_a\text{Al}_b\text{Ga}_{1-a-b}\text{N}$ ,  $0 \leq a$ ,  $0 \leq b$ ,  $a+b \leq 1$ ) is known as a material of light emitting devices, such as Light Emitting Diode, LD, etc. which emit light in ultraviolet - red. Using this semiconductor material, we announced blue Light Emitting Diode with a luminous intensity of 1 cd in November, 1993, announced the bluish green color Light Emitting Diode with a luminous intensity of 2 cds in April, 1994, and announced blue Light Emitting Diode with a luminous intensity of 2 cds in October, 1994. All of these Light Emitting Diodes are produced commercially, and practical use of the present display, a signal, etc. is presented with them.

[0003] The structure of the luminescence chip of the conventional blue and the bluish green color Light Emitting Diode which become drawing 2 from a nitride semiconductor is shown. It has the structure where the laminating of the buffer layer 22 which consists of GaN on a substrate 21, n type contact layer 23 which consists of n type GaN, n type clad layer 24 which consists of n type AlGaIn, the barrier layer 25 which consists of n type InGaIn, p type clad layer 26 which consists of p type AlGaIn, and the p type contact layer 27 which consists of p type GaN was fundamentally carried out to order. Acceptor impurity, such as donor impurities, such as Si and germanium, and/or Zn, Mg, is doped by n type InGaIn of a barrier layer 25, the luminescence wavelength of a Light Emitting Diode element is changing the kind of impurity which changes In composition ratio of InGaIn of the barrier layer, or is doped to a barrier layer, and it is possible to make it change to ultraviolet - red. For the moment, Light Emitting Diode with a luminescence wavelength of 510nm or less on which a donor impurity and acceptor impurity were simultaneously doped by the barrier layer is put in practical use.

[0004]

[Problem(s) to be Solved by the Invention] A radiant power output has about 3mW of the conventional Light Emitting Diodes by 20mA of forward currents, and they have the output of 20 times or more as compared with Light Emitting Diode which consists of SiC. However, when this Light Emitting Diode was low, for example, electrostatic pressure-proofing carried out bias of it and measured in the opposite direction, it had the fault that there were only 50-100V about. If Light

Emitting Diode is dealt with in the atmosphere dried when electrostatic pressure-proofing was low, since an element will be easily destroyed by static electricity, it is lacking in reliability.

[0005] Therefore, it is in accomplishing this invention in view of such a situation, and as for the place made into the purpose, electrostatic pressure-proofing realizing a large nitride semiconductor light emitting device and a high power light emitting device, and raising the reliability of a nitride semiconductor light emitting device.

[0006]

[Means for Solving the Problem] As a result of repeating various experiments about the nitride semiconductor light emitting device of terrorism structure to the conventional double, we trace that many of the causes are in p type clad layer grown up into the degree of a barrier layer, and came to accomplish this invention. The nitride semiconductor light emitting device of this invention namely, between the barrier layer which has a single quantum well or multiplex quantum well structure, and n type clad layer It has second n type clad layer which consists of an n type nitride semiconductor containing an indium, and is characterized by forming second p type clad layer which consists of a p type nitride semiconductor which contains an indium at least between the aforementioned barrier layer and p type clad layer, or p type GaN further.

[0007] Drawing 1 is the type section view showing the structure of the light emitting device concerning one example of this invention. This light emitting device shows the structure which carried out the laminating of a buffer layer 2, n type contact layer 3, n type clad layer 4, a barrier layer 5, second p type clad layer 6, first p type clad layer 6, and the p type contact layer 7 to order on the substrate 1.

[0008] The substrate of the nitride semiconductor and grid mismatching like SiC (6H and 4H are included), ZnO and Si besides sapphire (the Ath page, the Cth page, and the Rth page are included), and GaAs, a substrate with near nitride semiconductor which consists of an oxide single crystal like NGO (neodium gallate) and lattice constant, etc. can be used for a substrate 1.

[0009] As for a buffer layer 2, it is desirable to grow up GaN, AlN, GaAlN, etc. by 50A - 0.1 micrometers thickness, for example, according to the MOVPE method, it can be formed by making it grow up at 400 degrees C - 600 degrees C low temperature.

[0010] n type contact layer 3 is a layer which forms a negative electrode 8, it is desirable to grow up GaN, AlGaIn, InAlGaIn, etc. by 1 micrometer - 10 micrometers thickness, and the material of a negative electrode and desirable ohmic contact can be obtained by choosing GaN also in it. As a material of a negative electrode 8, aluminum, Au, Ti, etc. can be used preferably.

[0011] As for n type clad layer 4, it is desirable to grow up GaN, AlGaIn, InAlGaIn, etc. by 500A - 0.5 micrometers thickness, and a crystalline good layer is obtained by choosing GaN and AlGaIn also in it. Moreover, it is also possible to omit n type clad layer 4 or n type contact layer 3. If either is omitted, the layer which remained will act as n type clad layer and an n type contact layer.

[0012] As for a barrier layer 5, it is more desirable than a clad layer that bandgap energy sets the composition ratio of an indium to InGaIn changed suitably by the desired band gap especially that what is necessary is just nitride semiconductors, such as small InGaIn, InAlGaIn, and AlGaIn. Moreover, it is good also as multiplex quantum well structure which carried out the laminating of each thin film for the barrier layer 5 in combination, such as InGaIn/GaN and InGaIn/InGaIn (composition differs). single quantum well structure and multiplex quantum well structure -- which barrier layer -- also setting -- a barrier layer -- n type and p type -- although any are sufficient, it is desirable, especially when luminescence between bands with narrow half-value width, exciton luminescence, or quantum well level luminescence is obtained and a Light Emitting

Diode element and LD element are realized by considering especially as a non dope (additive-free) If a barrier layer is made into single quantum well (SQW:single quantum well) structure or multiplex quantum well (MQW:multiquantum well) structure, a light emitting device with a very high output will be obtained. It is the layer which pointed out the structure of a barrier layer where luminescence between the quantum level by InGaN of a non dope was obtained, in SQW and MQW, for example, constituted the barrier layer from InXGa1-XN ( $0 \leq X < 1$ ) of single composition at SQW, and strong luminescence between quantum level is obtained by making still more preferably 100Å or less of thickness of InXGa1-XN into 70Å or less. Moreover, MQW is taken as the multilayer which carried out two or more laminatings of the thin film of InXGa1-XN ( $X = 0$  and  $X = 1$  are included in this case) from which a composition ratio differs. Thus, luminescence to about 365nm - 660nm is obtained by luminescence between quantum level by setting a barrier layer to SQW and MQW. As well layer thickness of quantum structure, 70Å or less is desirable as mentioned above. Multiplex quantum well structure constitutes a well layer from InXGa1-XN, and, as for a barrier layer, it is desirable to constitute by InYGa1-YN (for  $Y = 0$  to be included in  $Y < X$  and this case) similarly. Since it can grow up at the same temperature if a well layer and a barrier layer are especially formed by InGaN preferably, a crystalline good barrier layer is obtained. If 150Å or less of thickness of a barrier layer is made into 120Å or less still more preferably, a high power light emitting device will be obtained. Moreover, you may dope a donor impurity and/or acceptor impurity to a barrier layer 5. If the crystallinity of the barrier layer which doped the impurity is the same as a non dope and a donor impurity will be doped, compared with the thing of a non dope, band luminescence intensity can be strengthened further. Although peak wavelength can be brought to about 0.5eV low energy side rather than the peak wavelength of luminescence between bands if acceptor impurity is doped, half-value width becomes large. If acceptor impurity and a donor impurity are doped simultaneously, luminescence intensity of the barrier layer which doped only acceptor impurity can be enlarged further. When realizing the barrier layer which doped especially acceptor impurity, as for the conductivity type of a barrier layer, it is desirable to dope donor impurities, such as Si, simultaneously and to consider as n type. A barrier layer 5 can be grown up by several angstroms - 0.5 micrometers thickness. However, when setting a barrier layer to SQW or MQW, it is desirable to form the n type nitride semiconductor containing In or second n type clad layer which consists of n type GaN between n type clad layer 4 and a barrier layer 5.

[0013] Next, it is necessary to form second p type clad layer 60 of this invention which is the feature most by the p type nitride semiconductor (InXAlYGa1-X-YN,  $0 < X$ ,  $Y \leq 0$ ,  $X+Y < 1$ ) which contains an indium at least, or p type GaN. Especially the thing to form with the nitride semiconductor which does not contain aluminum, such as InGaN or GaN, in it is desirable. As for the thickness of second p type clad layer 60, it is still more desirable still more preferably to form by thickness 100Å or less 200Å or less. It is because it becomes possible to raise electrostatic pressure-proofing of a light emitting device, maintaining most radiant power outputs of a light emitting device by adjusting to thickness 200Å or less. Conversely, when the thickness is thicker than 200Å, it is in the inclination for the output of a light emitting device to decline.

[0014] As for first p type clad layer 6, it is desirable to grow up GaN, AlGa<sub>N</sub>, InAlGa<sub>N</sub>, etc. by 500Å - 0.5 micrometers thickness, and a crystalline good layer is obtained by choosing GaN and AlGa<sub>N</sub> also in it. Moreover, when the composition of first p type clad layer 6 is the same as composition of second p type clad layer 60, the composition ratio of first p type clad layer 6 is changed, and bandgap energy is made the same as second p type clad layer 60, or it enlarges.

[0015] p type contact layer 7 is a layer which forms a positive electrode 9, for example, it is desirable to grow up GaN, AlGa<sub>N</sub>, InAlGa<sub>N</sub>, etc., and the material of a positive electrode and desirable ohmic contact can be obtained by choosing GaN also in it. As a positive-electrode material, nickel, Au, etc. can be used

preferably. Moreover, it is also possible to omit p type contact layer 7 or first p type clad layer 6. If either is omitted, the layer which remained will act as first p type clad layer and a p type contact layer.

[0016] The light emitting device of this invention is obtained using vapor growths, such as MOVPE (organic-metal vapor growth), MBE (molecular-beam vapor growth), and HDVPE (hydride vapor growth), by carrying out the laminating of  $\text{In}_a\text{Al}_b\text{Ga}_{1-a-b}\text{N}$  ( $0 \leq a$ ,  $0 \leq b$ ,  $a+b \leq 1$ ) by conductivity types, such as n type and p type, on a substrate. Although an n type nitride semiconductor is obtained also in the state of a non dope, it is obtained by introducing donor impurities, such as Si, germanium, and S, into a semiconductor layer into a crystal growth. The carrier concentration of n type layer can be adjusted by adjusting such donor impurity concentration. On the other hand, a p type nitride semiconductor layer is obtained by introducing acceptor impurity, such as Mg, Zn, Cd, calcium, Be, and C, into a semiconductor layer into a crystal growth similarly, or performing annealing above 400 degrees C after introduction. The carrier concentration of p type layer can be adjusted by adjusting these acceptor impurity concentration similarly. Although it is prepared in order that a buffer layer 2 may ease the grid mismatching of a substrate 1 and a nitride semiconductor, a buffer layer may not be formed in case the substrate which carried out grid adjustment with a nitride semiconductor like SiC and ZnO, and a substrate with a near lattice constant and a nitride semiconductor is used.

[0017]

[Function] In the conventional Light Emitting Diode, first p type clad layer containing aluminum was grown up on the barrier layer containing In. On the other hand, in this invention, second p type clad layer which consists of a nitride semiconductor which newly contains GaN or In between a barrier layer and first p type clad layer is grown up. Electrostatic pressure-proofing of a light emitting device can be raised by this composition. Second p type clad layer on a barrier layer carries out an operation of a buffer layer, and this improves the crystallinity of first p type clad layer, and is raising electrostatic pressure-proofing of an element. The nitride semiconductor has a property with the soft crystal itself in order of descending of bandgap energy, and  $\text{AlN} > \text{GaN} > \text{InN}$ . That is, compared with first p type clad layer with large bandgap energy, the crystal of the nitride semiconductor containing In or second p type clad layer which consists of GaN itself is softer than second p type clad layer. Since the crystallinity of first p type clad layer grown up on the second p type clad layer when second p type clad layer which is this soft crystal carries out an operation of a buffer layer becomes good and a lattice defect decreases, electrostatic pressure-proofing of the whole element improves.

[0018] The thickness of second p type clad layer which acts suitably as a buffer layer has desirable 200Å or less. Although electrostatic pressure-proofing tends to improve, when thickness is too thick, it is in the inclination for a crystal defect to occur mostly in the second p type clad layer itself, and to stop being able to act on it easily as a buffer layer, so that second p type clad layer is stacked thickly. If first p type clad layer is grown up on second p type clad layer with many crystal defects, since a crystal defect will get across even to first p type clad layer, first crystalline good p type clad layer stops being able to grow up easily. For this reason, when the thickness of second p type clad layer is too thick, it is in the inclination for the output of a light emitting device to decline. Especially the minimum of the thickness of second p type clad layer may not limit, and may be formed by several angstroms thickness which hits one atomic layer and two atomic layers.

[0019]

[Example] this invention is explained based on a concrete example below. The following examples show the growth method by the MOVPE method.

[0020] An example 1 is explained based on [example 1] drawing 1. First, the buffer layer 2 which becomes the Cth page of the silicon on sapphire 1 set to the reaction container from GaN at 500 degrees C is grown up by 500Å thickness using

TMG (trimethylgallium) and  $\text{NH}_3$ .

[0021] Next, temperature is raised to 1050 degrees C and TMG and n type contact layer 23 which consists of Si dope n type GaN using silane gas in addition to  $\text{NH}_3$  are grown up by 4-micrometer thickness.

[0022] Then, TMA (trimethylaluminum) is added to material gas and n type clad layer 4 which similarly consists of Si dope n mold aluminum $0.3\text{Ga}0.7\text{N}$  layer at 1050 degrees C is grown up by 0.1-micrometer thickness.

[0023] Next, temperature is lowered to 800 degrees C and the barrier layer 5 which consists of Si+Zn dope n type  $\text{In}0.05\text{Ga}0.95\text{N}$  is grown up by 0.1-micrometer thickness using TMG, TMI (trimethylindium),  $\text{NH}_3$ , silane gas, and DEZ (diethyl zinc).

[0024] Then, 50A of second p type clad layer 60 which consists of Mg dope p type  $\text{In}0.01\text{Ga}0.99\text{N}$  at 800 degrees C using TMG, TMI (trimethylindium),  $\text{NH}_3$ , and  $\text{Cp}2\text{Mg}$  (magnesium cyclopentadienyl) gas is grown up.

[0025] Next, temperature is raised to 1050 degrees C and first p type clad layer 6 which consists of Mg dope p type aluminum $0.3\text{Ga}0.7\text{N}$  is grown up by 0.1-micrometer thickness using TMG, TMA,  $\text{NH}_3$ , and  $\text{Cp}2\text{Mg}$  (magnesium cyclopentadienyl).

[0026] Then, p type contact layer 7 which consists of Mg dope p type GaN using TMG,  $\text{NH}_3$ , and  $\text{Cp}2\text{Mg}$  at 1050 degrees C is grown up by 0.5-micrometer thickness.

[0027] After a reaction end, temperature is lowered to a room temperature, a wafer is picked out from a reaction container, annealing of a wafer is performed at 700 degrees C, and p type layer is further formed into low resistance. Next, the mask of a predetermined configuration is formed in the front face of p type contact layer 7 of the best layer, and it \*\*\*\*\*s until the front face of n type contact layer 3 is exposed. The negative electrode 8 which becomes the front face of n type contact layer 3 from Ti and aluminum, and the positive electrode 9 which becomes the front face of p type contact layer 7 from nickel and Au are formed after etching. After electrode formation, after dividing a wafer into the chip of 350-micrometer angle, it considered as the Light Emitting Diode element. This Light Emitting Diode element showed with  $V_f 3.6\text{V}$ , 450nm of emission peak wavelengths, and a half-value width [ of 70nm ] blue luminescence by  $I_f 20\text{mA}$ , and the radiant power output was 3mW. Furthermore, when electrostatic pressure-proofing was measured having applied the reverse bias to the two electrodes of this Light Emitting Diode, an element did not break to 400V.

[0028] [Example 2] When thickness of second p type clad layer 60 was made into 100A and also the Light Emitting Diode element was obtained like the example 1, the radiant power output was the same as that of 3mW, and electrostatic pressure-proofing was improving to 450V.

[0029] [Example 3] When thickness of second p type clad layer 60 was made into 200A and also the Light Emitting Diode element was obtained like the example 1, 2.5mW and the electrostatic pressure-proofing of a radiant power output were improving to 550V.

[0030] [Example 4] Although electrostatic pressure-proofing improved to 650V when thickness of second p type clad layer 60 was made into 300A and also the Light Emitting Diode element was obtained like the example 1, the radiant power output declined to 1mW.

[0031] [Example 5] When Mg dope p type GaN was formed in second p type clad layer 60 by 10A thickness and also the Light Emitting Diode element was obtained like the example 1, the 3mW as an example 1 with the same radiant power output and electrostatic pressure-proofing were 360V.

[0032] [Example 6] drawing 3 is the typical cross section showing the structure of the light emitting device concerning an example 6. The place where this light emitting device differs from the light emitting device of drawing 1 is just going to form the n type nitride semiconductor which contains In as a new buffer layer, or second n type clad layer 40 which consists of n type GaN between n type clad layer 4 and a barrier layer 5. First n type clad layer 40

containing In and the barrier layer 5 containing In act as a buffer layer, and a crack does not go into n type clad layer 4 and p type clad layer 6, but this second clad layer 40 can grow with sufficient crystallinity, if it is desirable to form by thickness (10A or more and 0.1 micrometers or less) and it makes thickness of second n type clad layer 40 and a barrier layer 5 300A or more further. Furthermore, by growing up this second n type clad layer 40, the barrier layer which does not dope an impurity is realizable, half-value width is narrow and high luminescence of an output can be obtained.

[0033] This second n type clad layer 40 acts as a buffer layer between n type clad layers 4 containing a barrier layer 5, and aluminum and Ga. that is, the lattice constant of the n type clad layer 4 and the barrier layer 5 which contain aluminum and Ga since it has the property in which second n type clad layer 40 containing In and Ga is soft as a property of a crystal -- there is work which absorbs distortion produced according to a coefficient-of-thermal-expansion difference as it is irregular. Therefore, since a crack does not go into a barrier layer 5 and n type clad layer 4 considering a barrier layer 5 as SQW and MQW in which thickness has thin quantum structure, even if it makes a barrier layer into quantum structure, a barrier layer deforms elastically, and the crystal defect of a barrier layer decreases. That is, also in the state where the thickness of a barrier layer is thin, since the crystallinity of a barrier layer becomes good, a radiant power output increases. Furthermore, when the barrier layer made thickness thin, a radiant power output increases according to the quantum effect and the exciton effect. In other words, by the conventional light emitting device, it had prevented that a crack went into a clad layer and a barrier layer by thickening thickness of a single barrier layer with 1000A or more. However, since distortion by the coefficient-of-thermal-expansion difference and the stacking fault has always started the barrier layer and the thickness of a barrier layer is over the critical thickness which can deform elastically in the conventional light emitting device, it cannot deform elastically, but many crystal defects are produced in a barrier layer, and it seldom shines in luminescence between bands. By forming this second n type clad layer 40, it is possible in the barrier layer of quantum structure to raise the radiant power output of a light emitting device by leaps and bounds.

[0034] Specifically, after growing up n type clad layer 4 in an example 1, temperature is lowered to 800 degrees C and second n type clad layer 40 which consists of Si dope n type  $\text{In}_{0.01}\text{Ga}_{0.99}\text{N}$  is grown up by 500A thickness using TMG, TMI (trimethylindium),  $\text{NH}_3$ , and silane gas.

[0035] Then, the barrier layer 5 of the single quantum well structure which consists of non dope n type  $\text{In}_{0.05}\text{Ga}_{0.95}\text{N}$  at 800 degrees C using TMG, TMI, and  $\text{NH}_3$  is grown up by 80A thickness. When the rest grew up second p type clad layer 60, first p type clad layer 6, and p type contact layer 7 and was used as the Light Emitting Diode element like the example 1, this Light Emitting Diode element showed blue luminescence of Vf3.2V and 400nm of emission peak wavelengths by If20mA, and the radiant power output was 12mW. Furthermore, the half-value width of an emission spectrum is 20nm, and showed luminescence with very sufficient color purity. Moreover, it was 400V like [ electrostatic pressure-proofing ] the example 1.

[0036] In the [example 7] example 6, the barrier layer which becomes 25A from non dope  $\text{In}_{0.01}\text{Ga}_{0.99}\text{N}$  about the well layer which consists composition of a barrier layer 5 of non dope  $\text{In}_{0.05}\text{Ga}_{0.95}\text{N}$  is grown up by 50A thickness. This operation was repeated 13 times, the laminating of the well layer was carried out to the last, and the barrier layer 6 of 1000A of \*\*\*\* was grown up. When the rest grew up second p type clad layer 60, first p type clad layer 6, and p type contact layer 7 and was used as the Light Emitting Diode element like the example 1, this Light Emitting Diode element showed blue luminescence of Vf3.2V and 400nm of emission peak wavelengths by If20mA, and the radiant power output was 12mW. Furthermore, the half-value width of an emission spectrum is 20nm, and showed luminescence with very sufficient color purity. Moreover, electrostatic pressure-proofing was 500V. Rather than the barrier layer of single quantum well

structure, this shows that the direction of the element which has the barrier layer of multiplex quantum well structure has electrostatic high pressure-proofing.

[0037] Although the radiant power output declined to 3mW since, as for this Light Emitting Diode element, the thickness of a barrier layer became thick when thickness of the [example 8] barrier layer 5 was made into 500Å and also the Light Emitting Diode element was obtained like the example 6, it was 390nm of emission peak wavelengths, and with a half-value width [ of 20nm ] blue luminescence was shown, and electrostatic pressure-proofing was 400V.

[0038] [Example 9] When thickness of second p type clad layer 60 was made into 200Å and also the Light Emitting Diode element was obtained like the example 6, with 400nm of emission peak wavelengths and a half-value width [ of 20nm ] blue luminescence was shown as well as the example 6, and 10mW and the electrostatic pressure-proofing of a radiant power output were improving to 550V.

[0039]

[Effect of the Invention] In the conventional nitride semiconductor light emitting device, it was weak to electrostatic pressure-proofing, and in the environment dried especially, the element broke easily with static electricity, and it was lacking in reliability. However, since electrostatic pressure-proofing of a light emitting device improved by this invention, the element became that it is hard to be destroyed easily, and reliability improved extremely.

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#### TECHNICAL FIELD

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[Industrial Application] this invention relates to the nitride semiconductor light emitting device which starts the light emitting device which consists of a nitride semiconductor ( $\text{In}_a\text{Al}_b\text{Ga}_{1-a-b}\text{N}$ ,  $0 \leq a$ ,  $0 \leq b$ ,  $a+b \leq 1$ ) used for light emitting diode (Light Emitting Diode), a laser diode (LD), etc., especially has terrorism structure to double.

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#### PRIOR ART

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[Description of the Prior Art] The nitride semiconductor ( $\text{In}_a\text{Al}_b\text{Ga}_{1-a-b}\text{N}$ ,  $0 \leq a$ ,  $0 \leq b$ ,  $a+b \leq 1$ ) is known as a material of light emitting devices, such as Light Emitting Diode, LD, etc. which emit light in ultraviolet - red. Using this semiconductor material, we announced blue Light Emitting Diode with a luminous intensity of 1 cd in November, 1993, announced the bluish green color Light Emitting Diode with a luminous intensity of 2 cds in April, 1994, and announced blue Light Emitting Diode with a luminous intensity of 2 cds in October, 1994. All of these Light Emitting Diodes are produced commercially, and practical use of the present display, a signal, etc. is presented with them.

[0003] The structure of the luminescence chip of the conventional blue and the bluish green color Light Emitting Diode which become drawing 2 from a nitride semiconductor is shown. It has the structure where the laminating of the buffer layer 22 which consists of GaN on a substrate 21, n type contact layer 23 which consists of n type GaN, n type clad layer 24 which consists of n type AlGaIn, the barrier layer 25 which consists of n type InGaIn, p type clad layer 26 which consists of p type AlGaIn, and the p type contact layer 27 which consists of p type GaN was fundamentally carried out to order. Acceptor impurity, such as donor impurities, such as Si and germanium, and/or Zn, Mg, is doped by n type InGaIn of a barrier layer 25, the luminescence wavelength of a Light Emitting Diode element



is changing the kind of impurity which changes in composition ratio of InGaN of the barrier layer, or is doped to a barrier layer, and it is possible to make it change to ultraviolet - red. For the moment, Light Emitting Diode with a luminescence wavelength of 510nm or less on which a donor impurity and acceptor impurity were simultaneously doped by the barrier layer is put in practical use.

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#### EFFECT OF THE INVENTION

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[Effect of the Invention] In the conventional nitride semiconductor light emitting device, it was weak to electrostatic pressure-proofing, and in the environment dried especially, the element broke easily with static electricity, and it was lacking in reliability. However, since electrostatic pressure-proofing of a light emitting device improved by this invention, the element became that it is hard to be destroyed easily, and reliability improved extremely.

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#### TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] A radiant power output has about 3mW of the conventional Light Emitting Diodes by 20mA of forward currents, and they have the output of 20 times or more as compared with Light Emitting Diode which consists of SiC. However, when this Light Emitting Diode was low, for example, electrostatic pressure-proofing carried out bias of it and measured in the opposite direction, it had the fault that there were only 50-100V about. If Light Emitting Diode is dealt with in the atmosphere dried when electrostatic pressure-proofing was low, since an element will be easily destroyed by static electricity, it is lacking in reliability.

[0005] Therefore, it is in accomplishing this invention in view of such a situation, and as for the place made into the purpose, electrostatic pressure-proofing realizing a large nitride semiconductor light emitting device and a high power light emitting device, and raising the reliability of a nitride semiconductor light emitting device.

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#### MEANS

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[Means for Solving the Problem] As a result of repeating various experiments about the nitride semiconductor light emitting device of terrorism structure to the conventional double, we trace that many of the causes are in p type clad layer grown up into the degree of a barrier layer, and came to accomplish this invention. The nitride semiconductor light emitting device of this invention namely, between the barrier layer which has a single quantum well or multiplex quantum well structure, and n type clad layer It has second n type clad layer which consists of an n type nitride semiconductor containing an indium, and is characterized by forming second p type clad layer which consists of a p type nitride semiconductor which contains an indium at least between the aforementioned barrier layer and p type clad layer, or p type GaN further.

[0007] Drawing 1 is the type section view showing the structure of the light emitting device concerning one example of this invention. This light emitting device shows the structure which carried out the laminating of a buffer layer 2, n type contact layer 3, n type clad layer 4, a barrier layer 5, second p type clad layer 6, first p type clad layer 6, and the p type contact layer 7 to order



on the substrate 1.

[0008] The substrate of the nitride semiconductor and grid mismatching like SiC (6H and 4H are included), ZnO and Si besides sapphire (the Ath page, the Cth page, and the Rth page are included), and GaAs, a substrate with near nitride semiconductor which consists of an oxide single crystal like NGO (neodium gallate) and lattice constant, etc. can be used for a substrate 1.

[0009] As for a buffer layer 2, it is desirable to grow up GaN, AlN, GaAlN, etc. by 50A - 0.1 micrometers thickness, for example, according to the MOVPE method, it can be formed by making it grow up at 400 degrees C - 600 degrees C low temperature.

[0010] n type contact layer 3 is a layer which forms a negative electrode 8, it is desirable to grow up GaN, AlGaIn, InAlGaIn, etc. by 1 micrometer - 10 micrometers thickness, and the material of a negative electrode and desirable ohmic contact can be obtained by choosing GaN also in it. As a material of a negative electrode 8, aluminum, Au, Ti, etc. can be used preferably.

[0011] As for n type clad layer 4, it is desirable to grow up GaN, AlGaIn, InAlGaIn, etc. by 500A - 0.5 micrometers thickness, and a crystalline good layer is obtained by choosing GaN and AlGaIn also in it. Moreover, it is also possible to omit n type clad layer 4 or n type contact layer 3. If either is omitted, the layer which remained will act as n type clad layer and an n type contact layer.

[0012] As for a barrier layer 5, it is more desirable than a clad layer that bandgap energy sets the composition ratio of an indium to InGaIn changed suitably by the desired band gap especially that what is necessary is just nitride semiconductors, such as small InGaIn, InAlGaIn, and AlGaIn. Moreover, it is good also as multiplex quantum well structure which carried out the laminating of each thin film for the barrier layer 5 in combination, such as InGaIn/GaN and InGaIn/InGaIn (composition differs). single quantum well structure and multiplex quantum well structure -- which barrier layer -- also setting -- a barrier layer -- n type and p type -- although any are sufficient, it is desirable, especially when luminescence between bands with narrow half-value width, exciton luminescence, or quantum well level luminescence is obtained and a Light Emitting Diode element and LD element are realized by considering especially as a non dope (additive-free) If a barrier layer is made into single quantum well (SQW:single quantum well) structure or multiplex quantum well (MQW:multiquantum well) structure, a light emitting device with a very high output will be obtained. It is the layer which pointed out the structure of a barrier layer where luminescence between the quantum level by InGaIn of a non dope was obtained, in SQW and MQW, for example, constituted the barrier layer from InXGa1-XN ( $0 < X < 1$ ) of single composition at SQW, and strong luminescence between quantum level is obtained by making still more preferably 100A or less of thickness of InXGa1-XN into 70A or less. Moreover, MQW is taken as the multilayer which carried out two or more laminatings of the thin film of InXGa1-XN ( $X = 0$  and  $X = 1$  are included in this case) from which a composition ratio differs. Thus, luminescence to about 365nm - 660nm is obtained by luminescence between quantum level by setting a barrier layer to SQW and MQW. As well layer thickness of quantum structure, 70A or less is desirable as mentioned above. Multiplex quantum well structure constitutes a well layer from InXGa1-XN, and, as for a barrier layer, it is desirable to constitute by InYGa1-YN (for  $Y = 0$  to be included in  $Y < X$  and this case) similarly. Since it can grow up at the same temperature if a well layer and a barrier layer are especially formed by InGaIn preferably, a crystalline good barrier layer is obtained. If 150A or less of thickness of a barrier layer is made into 120A or less still more preferably, a high power light emitting device will be obtained. Moreover, you may dope a donor impurity and/or acceptor impurity to a barrier layer 5. If the crystallinity of the barrier layer which doped the impurity is the same as a non dope and a donor impurity will be doped, compared with the thing of a non dope, band luminescence intensity can be strengthened further. Although peak wavelength can be brought to about 0.5eV low

energy side rather than the peak wavelength of luminescence between bands if acceptor impurity is doped, half-value width becomes large. If acceptor impurity and a donor impurity are doped simultaneously, luminescence intensity of the barrier layer which doped only acceptor impurity can be enlarged further. When realizing the barrier layer which doped especially acceptor impurity, as for the conductivity type of a barrier layer, it is desirable to dope donor impurities, such as Si, simultaneously and to consider as n type. A barrier layer 5 can be grown up by several angstroms - 0.5 micrometers thickness. However, when setting a barrier layer to SQW or MQW, it is desirable to form the n type nitride semiconductor containing In or second n type clad layer which consists of n type GaN between n type clad layer 4 and a barrier layer 5.

[0013] Next, it is necessary to form second p type clad layer 60 of this invention which is the feature most by the p type nitride semiconductor ( $\text{In}_x\text{Al}_y\text{Ga}_{1-x-y}\text{N}$ ,  $0 < x$ ,  $y \leq 0$ ,  $x+y < 1$ ) which contains an indium at least, or p type GaN. Especially the thing to form with the nitride semiconductor which does not contain aluminum, such as InGaN or GaN, in it is desirable. As for the thickness of second p type clad layer 60, it is still more desirable still more preferably to form by thickness 100Å or less 200Å or less. It is because it becomes possible to raise electrostatic pressure-proofing of a light emitting device, maintaining most radiant power outputs of a light emitting device by adjusting to thickness 200Å or less. Conversely, when the thickness is thicker than 200Å, it is in the inclination for the output of a light emitting device to decline.

[0014] As for first p type clad layer 6, it is desirable to grow up GaN, AlGaN, InAlGaN, etc. by 500Å - 0.5 micrometers thickness, and a crystalline good layer is obtained by choosing GaN and AlGaN also in it. Moreover, when the composition of first p type clad layer 6 is the same as composition of second p type clad layer 60, the composition ratio of first p type clad layer 6 is changed, and bandgap energy is made the same as second p type clad layer 60, or it enlarges.

[0015] p type contact layer 7 is a layer which forms a positive electrode 9, for example, it is desirable to grow up GaN, AlGaN, InAlGaN, etc., and the material of a positive electrode and desirable ohmic contact can be obtained by choosing GaN also in it. As a positive-electrode material, nickel, Au, etc. can be used preferably. Moreover, it is also possible to omit p type contact layer 7 or first p type clad layer 6. If either is omitted, the layer which remained will act as first p type clad layer and a p type contact layer.

[0016] The light emitting device of this invention is obtained using vapor growths, such as MOVPE (organic-metal vapor growth), MBE (molecular-beam vapor growth), and HDVPE (hydride vapor growth), by carrying out the laminating of  $\text{In}_a\text{Al}_b\text{Ga}_{1-a-b}\text{N}$  ( $0 \leq a$ ,  $0 \leq b$ ,  $a+b \leq 1$ ) by conductivity types, such as n type and p type, on a substrate. Although an n type nitride semiconductor is obtained also in the state of a non dope, it is obtained by introducing donor impurities, such as Si, germanium, and S, into a semiconductor layer into a crystal growth. The carrier concentration of n type layer can be adjusted by adjusting such donor impurity concentration. On the other hand, a p type nitride semiconductor layer is obtained by introducing acceptor impurity, such as Mg, Zn, Cd, calcium, Be, and C, into a semiconductor layer into a crystal growth similarly, or performing annealing above 400 degrees C after introduction. The carrier concentration of p type layer can be adjusted by adjusting these acceptor impurity concentration similarly. Although it is prepared in order that a buffer layer 2 may ease the grid mismatching of a substrate 1 and a nitride semiconductor, a buffer layer may not be formed in case the substrate which carried out grid adjustment with a nitride semiconductor like SiC and ZnO, and a substrate with a near lattice constant and a nitride semiconductor is used.

[Function] In the conventional Light Emitting Diode, first p type clad layer containing aluminum was grown up on the barrier layer containing In. On the other hand, in this invention, second p type clad layer which consists of a nitride semiconductor which newly contains GaN or In between a barrier layer and first p type clad layer is grown up. Electrostatic pressure-proofing of a light emitting device can be raised by this composition. Second p type clad layer on a barrier layer carries out an operation of a buffer layer, and this improves the crystallinity of first p type clad layer, and is raising electrostatic pressure-proofing of an element. The nitride semiconductor has a property with the soft crystal itself in order of descending of bandgap energy, and  $\text{AlN} > \text{GaN} > \text{InN}$ . That is, compared with first p type clad layer with large bandgap energy, the crystal of the nitride semiconductor containing In or second p type clad layer which consists of GaN itself is softer than second p type clad layer. Since the crystallinity of first p type clad layer grown up on the second p type clad layer when second p type clad layer which is this soft crystal carries out an operation of a buffer layer becomes good and a lattice defect decreases, electrostatic pressure-proofing of the whole element improves.

[0018] The thickness of second p type clad layer which acts suitably as a buffer layer has desirable 200Å or less. Although electrostatic pressure-proofing tends to improve, when thickness is too thick, it is in the inclination for a crystal defect to occur mostly in the second p type clad layer itself, and to stop being able to act on it easily as a buffer layer, so that second p type clad layer is stacked thickly. If first p type clad layer is grown up on second p type clad layer with many crystal defects, since a crystal defect will get across even to first p type clad layer, first crystalline good p type clad layer stops being able to grow up easily. For this reason, when the thickness of second p type clad layer is too thick, it is in the inclination for the output of a light emitting device to decline. Especially the minimum of the thickness of second p type clad layer may not limit, and may be formed by several angstroms thickness which hits one atomic layer and two atomic layers.

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#### EXAMPLE

[Example] this invention is explained based on a concrete example below. The following examples show the growth method by the MOVPE method.

[0020] An example 1 is explained based on [example 1] drawing 1. First, the buffer layer 2 which becomes the Cth page of the silicon on sapphire 1 set to the reaction container from GaN at 500 degrees C is grown up by 500Å thickness using TMG (trimethylgallium) and  $\text{NH}_3$ .

[0021] Next, temperature is raised to 1050 degrees C and TMG and n type contact layer 23 which consists of Si dope n type GaN using silane gas in addition to  $\text{NH}_3$  are grown up by 4-micrometer thickness.

[0022] Then, TMA (trimethylaluminum) is added to material gas and n type clad layer 4 which similarly consists of Si dope n mold aluminum $0.3\text{Ga}0.7\text{N}$  layer at 1050 degrees C is grown up by 0.1-micrometer thickness.

[0023] Next, temperature is lowered to 800 degrees C and the barrier layer 5 which consists of Si+Zn dope n type  $\text{In}0.05\text{Ga}0.95\text{N}$  is grown up by 0.1-micrometer thickness using TMG, TMI (trimethylindium),  $\text{NH}_3$ , silane gas, and DEZ (diethyl zinc).

[0024] Then, 50Å of second p type clad layer 60 which consists of Mg dope p type  $\text{In}0.01\text{Ga}0.99\text{N}$  at 800 degrees C using TMG, TMI (trimethylindium),  $\text{NH}_3$ , and  $\text{Cp}2\text{Mg}$  (magnesium cyclopentadienyl) gas is grown up.

[0025] Next, temperature is raised to 1050 degrees C and first p type clad layer 6 which consists of Mg dope p type aluminum $0.3\text{Ga}0.7\text{N}$  is grown up by 0.1-micrometer thickness using TMG, TMA,  $\text{NH}_3$ , and  $\text{Cp}2\text{Mg}$  (magnesium cyclopentadienyl).

[0026] Then, p type contact layer 7 which consists of Mg dope p type GaN using TMG, NH<sub>3</sub>, and Cp<sub>2</sub>Mg at 1050 degrees C is grown up by 0.5-micrometer thickness.

[0027] After a reaction end, temperature is lowered to a room temperature, a wafer is picked out from a reaction container, annealing of a wafer is performed at 700 degrees C, and p type layer is further formed into low resistance. Next, the mask of a predetermined configuration is formed in the front face of p type contact layer 7 of the best layer, and it \*\*\*\*\*s until the front face of n type contact layer 3 is exposed. The negative electrode 8 which becomes the front face of n type contact layer 3 from Ti and aluminum, and the positive electrode 9 which becomes the front face of p type contact layer 7 from nickel and Au are formed after etching. After electrode formation, after dividing a wafer into the chip of 350-micrometer angle, it considered as the Light Emitting Diode element. This Light Emitting Diode element showed with Vf3.6V, 450nm of emission peak wavelengths, and a half-value width [ of 70nm ] blue luminescence by If20mA, and the radiant power output was 3mW. Furthermore, when electrostatic pressure-proofing was measured having applied the reverse bias to the two electrodes of this Light Emitting Diode, an element did not break to 400V.

[0028] [Example 2] When thickness of second p type clad layer 60 was made into 100A and also the Light Emitting Diode element was obtained like the example 1, the radiant power output was the same as that of 3mW, and electrostatic pressure-proofing was improving to 450V.

[0029] [Example 3] When thickness of second p type clad layer 60 was made into 200A and also the Light Emitting Diode element was obtained like the example 1, 2.5mW and the electrostatic pressure-proofing of a radiant power output were improving to 550V.

[0030] [Example 4] Although electrostatic pressure-proofing improved to 650V when thickness of second p type clad layer 60 was made into 300A and also the Light Emitting Diode element was obtained like the example 1, the radiant power output declined to 1mW.

[0031] [Example 5] When Mg dope p type GaN was formed in second p type clad layer 60 by 10A thickness and also the Light Emitting Diode element was obtained like the example 1, the 3mW as an example 1 with the same radiant power output and electrostatic pressure-proofing were 360V.

[0032] [Example 6] drawing 3 is the typical cross section showing the structure of the light emitting device concerning an example 6. The place where this light emitting device differs from the light emitting device of drawing 1 is just going to form the n type nitride semiconductor which contains In as a new buffer layer, or second n type clad layer 40 which consists of n type GaN between n type clad layer 4 and a barrier layer 5. First n type clad layer 40 containing In and the barrier layer 5 containing In act as a buffer layer, and a crack does not go into n type clad layer 4 and p type clad layer 6, but this second clad layer 40 can grow with sufficient crystallinity, if it is desirable to form by thickness (10A or more and 0.1 micrometers or less) and it makes thickness of second n type clad layer 40 and a barrier layer 5 300A or more further. Furthermore, by growing up this second n type clad layer 40, the barrier layer which does not dope an impurity is realizable, half-value width is narrow and high luminescence of an output can be obtained.

[0033] This second n type clad layer 40 acts as a buffer layer between n type clad layers 4 containing a barrier layer 5, and aluminum and Ga. that is, the lattice constant of the n type clad layer 4 and the barrier layer 5 which contain aluminum and Ga since it has the property in which second n type clad layer 40 containing In and Ga is soft as a property of a crystal -- there is work which absorbs distortion produced according to a coefficient-of-thermal-expansion difference as it is irregular. Therefore, since a crack does not go into a barrier layer 5 and n type clad layer 4 considering a barrier layer 5 as SQW and MQW in which thickness has thin quantum structure, even if it makes a barrier layer into quantum structure, a barrier layer deforms elastically, and the crystal defect of

a barrier layer decreases. That is, also in the state where the thickness of a barrier layer is thin, since the crystallinity of a barrier layer becomes good, a radiant power output increases. Furthermore, when the barrier layer made thickness thin, a radiant power output increases according to the quantum effect and the exciton effect. In other words, by the conventional light emitting device, it had prevented that a crack went into a clad layer and a barrier layer by thickening thickness of a single barrier layer with 1000A or more. However, since distortion by the coefficient-of-thermal-expansion difference and the stacking fault has always started the barrier layer and the thickness of a barrier layer is over the critical thickness which can deform elastically in the conventional light emitting device, it cannot deform elastically, but many crystal defects are produced in a barrier layer, and it seldom shines in luminescence between bands. By forming this second n type clad layer 40, it is possible in the barrier layer of quantum structure to raise the radiant power output of a light emitting device by leaps and bounds.

[0034] Specifically, after growing up n type clad layer 4 in an example 1, temperature is lowered to 800 degrees C and second n type clad layer 40 which consists of Si dope n type In<sub>0.01</sub>Ga<sub>0.99</sub>N is grown up by 500A thickness using TMG, TMI (trimethylindium), NH<sub>3</sub>, and silane gas.

[0035] Then, the barrier layer 5 of the single quantum well structure which consists of non dope n type In<sub>0.05</sub>Ga<sub>0.95</sub>N at 800 degrees C using TMG, TMI, and NH<sub>3</sub> is grown up by 80A thickness. When the rest grew up second p type clad layer 60, first p type clad layer 6, and p type contact layer 7 and was used as the Light Emitting Diode element like the example 1, this Light Emitting Diode element showed blue luminescence of Vf3.2V and 400nm of emission peak wavelengths by If20mA, and the radiant power output was 12mW. Furthermore, the half-value width of an emission spectrum is 20nm, and showed luminescence with very sufficient color purity. Moreover, it was 400V like [ electrostatic pressure-proofing ] the example 1.

[0036] In the [example 7] example 6, the barrier layer which becomes 25A from non dope In<sub>0.01</sub>Ga<sub>0.99</sub>N about the well layer which consists composition of a barrier layer 5 of non dope In<sub>0.05</sub>Ga<sub>0.95</sub>N is grown up by 50A thickness. This operation was repeated 13 times, the laminating of the well layer was carried out to the last, and the barrier layer 6 of 1000A of \*\*\*\* was grown up. When the rest grew up second p type clad layer 60, first p type clad layer 6, and p type contact layer 7 and was used as the Light Emitting Diode element like the example 1, this Light Emitting Diode element showed blue luminescence of Vf3.2V and 400nm of emission peak wavelengths by If20mA, and the radiant power output was 12mW. Furthermore, the half-value width of an emission spectrum is 20nm, and showed luminescence with very sufficient color purity. Moreover, electrostatic pressure-proofing was 500V. Rather than the barrier layer of single quantum well structure, this shows that the direction of the element which has the barrier layer of multiplex quantum well structure has electrostatic high pressure-proofing.

[0037] Although the radiant power output declined to 3mW since, as for this Light Emitting Diode element, the thickness of a barrier layer became thick when thickness of the [example 8] barrier layer 5 was made into 500A and also the Light Emitting Diode element was obtained like the example 6, it was 390nm of emission peak wavelengths, and with a half-value width [ of 20nm ] blue luminescence was shown, and electrostatic pressure-proofing was 400V.

[0038] [Example 9] When thickness of second p type clad layer 60 was made into 200A and also the Light Emitting Diode element was obtained like the example 6, with 400nm of emission peak wavelengths and a half-value width [ of 20nm ] blue luminescence was shown as well as the example 6, and 10mW and the electrostatic pressure-proofing of a radiant power output were improving to 550V.

## DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The type section view showing the structure of the light emitting device concerning one example of this invention.

[Drawing 2] The type section view showing the structure of the conventional light emitting device.

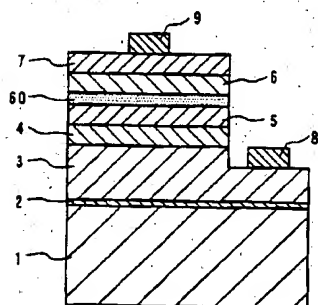
[Drawing 3] The type section view showing the structure of the light emitting device concerning other examples of this invention.

[Description of Notations]

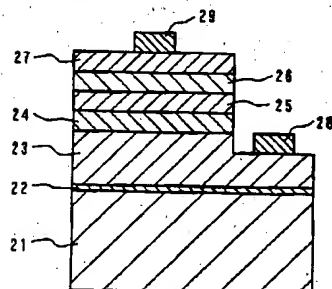
- 1 .... Substrate
- 2 .... Buffer layer
- 3 .... n type contact layer
- 4 .... n type clad layer
- 5 .... Barrier layer
- 60 .... Second p type clad layer
- 6 .... First p type clad layer
- 7 .... p type contact layer
- 8 .... Negative electrode
- 9 .... Positive electrode

## DRAWINGS

[Drawing 1]



[Drawing 2]



[Drawing 3]

